# Fermi level quantum numbers and secondary gap of conducting carbon nanotubes

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**Abstract**

For the single-wall carbon nanotubes conducting in the simplest tight binding model, the complete set of line group symmetry based quantum numbers for the bands crossing at Fermi level are given. Besides linear ($k$), helical ($\tilde{k}$ and angular momenta, emerging from roto-translational symmetries, the parities of $U$ axis and (in the zig-zag and armchair cases only) mirror planes appear in the assignation. The helical and angular momentum quantum numbers of the crossing bands never vanishes, what supports proposed chirality of currents. Except for the armchair tubes, the crossing bands have the same quantum numbers and, according to the non-crossing rule, a secondary gap arises, as it is shown by the accurate tight-binding calculation. In the armchair case the different vertical mirror parity of the crossing bands provides substantial conductivity, though $k_{\mathrm{F}}$ is slightly decreased.

*Key words:* Nanotubes, Conductivity, Symmetry

Since their discovery [1] conducting properties of carbon nanotubes have been extensively studied, due to expected technological applications [2]. The electronic bands have been found within the tight binding approximation and assigned either by the linear $k$ and the angular $m$ quasi momenta quantum numbers [3, 4], or by the quantum numbers $\tilde{k}$ and $\tilde{m}$ of the helical and "pure" (i.e. the remnant being not coupled to translations) angular momentum [5, 6]. The both sets of quantum numbers reflect translational and rotational tube symmetries [7], forming the group $\boldsymbol{L}^{(1)}$. The local curvature has been partly neglected in these calculations, assuming the same interaction of carbon atom with its three neighbors. This model predicts [3, 5, 9] that tube $(n_1, n_2)$ is conducting whenever $n_1 - n_2$ is multiple of 3, what is well experimentally justified [8]. It is also suggested [3, 5] that even in this case the local curvature opens a small secondary gap (less then 0.01 eV and decreasing with the square of the

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tube diameter [9]) when $n_1 - n_2$ is non-vanishing; this feature seems to be still beyond the experimental precision.

Here, we present the full set of symmetry quantum numbers of the bands crossing at the Fermi level within the mentioned simple model. They are used to show that the symmetry gives the most profound and easy prediction of the opening of the secondary gap: non-crossing rule prevents conductivity in all but the armchair tubes. The conductivity of the later is due to the extra parity contained in the recently determined [7] full symmetry group, which makes non-crossing rule inapplicable. Finally, the secondary gap is estimated within a distortion sensitive tight-binding model.

The tube $(n_1, n_2)$ is translationally periodic along the tube axis, with period $a = a_0\sqrt{3q/2n\mathcal{R}}$ ($a_0 = 2.461$Å), where $n$ is the greatest common divisor of $n_1$ and $n_2$, $q = 2(n_1^2+n_1n_2+n_2^2)/n\mathcal{R}$ and $\mathcal{R} = 3$ if $(n_1-n_2)/n$ is multiple of 3 while $\mathcal{R} = 1$ otherwise. The tube is also invariant under rotations for $2\pi/n$ around the tube axis. These roto-translational symmetries form the group $\boldsymbol{L}^{(1)}$. In addition, chiral ($\mathcal{C}$) tubes have horizontal $U$-axis (rotation for $\pi$ around the $x$-axis; Fig. 1), doubling the former group:

$$\boldsymbol{L}_{\mathcal{C}} = \boldsymbol{T}_q^r \boldsymbol{D}_n = \boldsymbol{L}^{(1)} + U\boldsymbol{L}^{(1)}. \tag{1a}$$

Here, the parameter defining the screw-axis (helical) group $\boldsymbol{T}_q^r$ is

$$r = \frac{q}{n}\mathrm{Fr}\left[\frac{n}{q\mathcal{R}}(3 - 2\frac{n_1 - n_2}{n_1}) + \frac{n}{n_1}\left(\frac{n_1 - n_2}{n}\right)^{\varphi(\frac{n_1}{n})-1}\right]$$

(Fr denotes the fractional part and $\varphi$ the Euler function). Zig-zag ($\mathcal{Z}$, with $\mathcal{R} = 1$) and armchair ($\mathcal{A}$, $\mathcal{R} = 3$) tubes, $(n, 0)$ and $(n, n)$ also have vertical mirror planes $\sigma_x$ (the other symmetry elements are generated from the mentioned ones), which doubles the group $\boldsymbol{L}_{\mathcal{C}}$ (in these cases $q = 2n$ and $r = 1$):

$$\boldsymbol{L}_{\mathcal{ZA}} = \boldsymbol{T}_{2n}^1 \boldsymbol{D}_{nh} = \boldsymbol{L}_{\mathcal{C}} + \sigma_x \boldsymbol{L}_{\mathcal{C}}. \tag{1b}$$

The additional $U$ and $\sigma_x$ symmetries yield new conserved quantum numbers: $+$ and $-$ ($A$ and $B$) denote even and odd states with respect to the $U$-axis ($\sigma_x$ plane). The electronic bands assignation by the complete set of conserved quantum numbers makes easier theoretical predictions of their degeneracies and selection rules relevant for the various physical processes. Here we perform this task for the bands necessary to discuss the conductivity.

The tight binding hamiltonian with single atomic $p$-orbital $|i\rangle$ per $i$-th site encountering only the nearest neighbors interaction is $H = \frac{1}{2}\sum_s \sum_{i=1}^3 V_i \, |s\rangle\langle s, i|$, with $i$ running over the neighbors of the $s$-th C atom (Fig. 1). Neglecting the local curvature, i.e. taking $V_i = V$ (estimated between $-3$eV and $-2.5$eV),

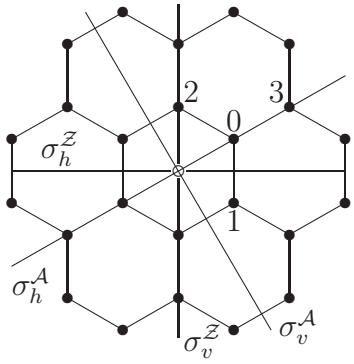


Fig. 1. Nearest neighbors of the C-atom atom denoted by 0, are the atoms 1, 2 and 3. Perpendicular to the figure at $\circ$ is $U$-axis, while $\sigma_{h/v}^{\mathcal{Z}/\mathcal{A}}$ stands for vertical and horizontal mirror planes of $\mathcal{Z}$ and $\mathcal{A}$ tubes.

the band structure of such simplified hamiltonian $H^0$ can be found easily [3, 4, 5]. The assignation by the full line group quantum numbers has been performed recently [10]. In particular, for the tubes with integer $(n_1 - n_2)/3$, there are pairs of bands crossing at Fermi level $E_{\rm F} = 0$. These bands and their intersection point are characterized by the quantum numbers given in table 1.

Table 1
The quantum numbers at Fermi level. Both cases of $\tilde{m}_{\rm F}$ are gathered in $\tilde{m}_{\rm F} \doteq \frac{2}{3} nr\mathcal{R}$, with equality modulo the interval $(-n/2, n/2]$.

| | $\mathcal{C}$: $\mathcal{R}=3$ | $\mathcal{R}=1$ | $\mathcal{Z}$ | $\mathcal{A}$ | $\mathcal{C}$: $\mathcal{R}=3$ | $\mathcal{R}=1$ |
|---|---|---|---|---|---|---|
| $k_{\rm F}$ | $\frac{2\pi}{3a}$ | 0 | 0 | $\frac{2\pi}{3a}$ | $\tilde{k}_F$ | $\frac{2q\pi}{3na}$ |
| $m_{\rm F}$ | $nr \pmod q$ | $\pm\frac{q}{3}$ | $\frac{2n}{3}$ | $n$ | $\tilde{m}_{\rm F}$ 0 | $\frac{n}{3}(-1)^{{\rm Fr}(r/3)}$ |

For $\mathcal{C}$ tubes, the simpler to handle with set of quantum numbers, $\tilde{k}_{\rm F}$ and $\tilde{m}_{\rm F}$, is used. Introducing the angles

$$\tilde{\psi}_1 = -\tilde{k}a\frac{n_2}{q} + 4r\pi\frac{2n_1 + (1+r\mathcal{R})n_2}{3q}, \tag{2a}$$

$$\tilde{\psi}_2 = \tilde{k}a\frac{n_1}{q} + 4r\pi\frac{(1-r\mathcal{R})n_1 + 2n_2}{3q}, \tag{2b}$$

$$\tilde{\psi}_3 = \tilde{\psi}_2 - \tilde{\psi}_1, \tag{2c}$$

the Fermi bands for $\mathcal{C}$, $\mathcal{Z}$ and $\mathcal{A}$ conducting tubes are:

$$E_{\mathcal{C}}(\tilde{k}) = \pm V\sqrt{3 + 2\sum_i \cos\tilde{\psi}_i}, \tag{3a}$$

$$G_{\mathcal{Z}}(k) = \pm V\sqrt{2(1 - \cos\frac{ka}{2})}, \tag{3b}$$

$$E_{\mathcal{A}}^{A/B}(k) = \pm V(1 - 2\cos\frac{ka}{2}). \tag{3c}$$

In the irreducible domain $\tilde{k} \in [0, q\pi/na]$ of the Brillouine zone [11], the both bands $E_{\mathcal{C}}(\tilde{k})$ correspond to the same two dimensional irreducible representation ${}_{\tilde{k}}E_{\tilde{m}_{\rm F}}$ of the group (1a), [12]. On the contrary, two bands $E^A_{\mathcal{A}}(k)$ and $E^A_{\mathcal{A}}(k)$ (in the irreducible domain $k \in [0, \pi/a]$) correspond to different two dimensional representations ${}_kE^A_n$ and ${}_kE^B_n$ of the group (1b), [10]. As for the $\mathcal{Z}$ tubes, the both bands $G_{\mathcal{Z}}(k)$ correspond to the four fold representation ${}_kG_{2n/3}$ of the group (1b). These two bands cross at $k_{\rm F} = 0$, giving raise to four fold degeneracy of Fermi level being spanned by two pairs of states carrying representations ${}_0E^+_{2n/3}$ and ${}_0E^-_{2n/3}$ of different $U$ parities.

The non-crossing rule [13] asserts that the bands assigned by the same values of complete set of symmetry based quantum numbers may not cross (or touch). In fact, it can be easily derived from the Wigner-Eckart theorem that in such a case more accurate approach (retaining geometrical symmetry of the model) results in the gap opening at the crossing points. Therefore, in a higher order approximation, $\mathcal{C}$ tubes attain a gap at $\tilde{k}_{\rm F}$; the same argument prevents crossing in any other $\tilde{k}$. Further, although at $k_{\rm F} = 0$ the non-crossing rule at first glance does not obstruct the conductivity of $\mathcal{Z}$ tubes, the finite gap between the bands $G^{\pm}_{\mathcal{Z}}$ along the zone implies, by continuity argument, that a gap arises at $k_{\rm F} = 0$, too. On the contrary, the relevant $\mathcal{A}$ tube bands have different parities along Brillouine zone, being thus beyond the scope of the non-crossing rule. In fact, in all these cases the "accidental" degeneracy at $k_{\rm F}$ reflects the increased symmetry tacitly imposed by modeling the interatomic interactions by mutually equal constants $V_i$: the hamiltonian became additionally invariant under the permutations of the neighboring atoms. As the following analysis shows, this artefact of the model is to disappear in a more precise approach obeying the original symmetry.

The high symmetry of the nanotubes enables to get the exact dispersion relations for the tight-binding calculations [10] with arbitrary chosen interaction coefficients $V_i$:

$$E_{\mathcal{C}}(\tilde{k}) = \pm\sqrt{\sum_i (V_i^2 + 2\frac{V_1V_2V_3}{V_i}\cos\tilde{\psi}_i)}, \tag{4a}$$

$$G_{\mathcal{Z}}(k) = \pm\sqrt{V_1^2 + V_2^2 - 2V_1V_2\cos\frac{ka}{2}}, \tag{4b}$$

$$E^{A/B}_{\mathcal{A}}(k) = \pm(V_3 - 2V_1\cos\frac{ka}{2}). \tag{4c}$$

To make the model realistic, the coefficients should be proportional to the overlap integrals [14, 15] of the site $p^{\perp}$ orbitals, meaning that the first order correction to $V_i$ is proportional to the bond length $d_i$ variation. Especially, $V_0 = V_1 < V_2 = V_3$ for $\mathcal{Z}$ and $V_1 = V_2 < V_3$ for $\mathcal{A}$ tubes. The calculation made

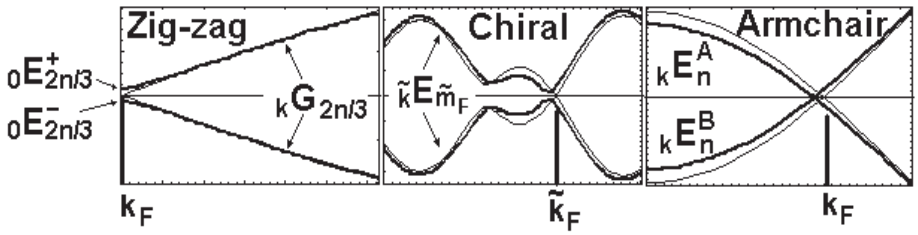


Fig. 2. Bands (3) are crossed at $k_{\mathrm{F}}$ (thin lines), while the corresponding bands (4) attain a gap (thick lines), unless in the armchair case when the crossing point is shifted to the left. The representations corresponding to the bands are given.

with such class of interaction confirm the appearance of the gap (fig. 2). It decreases with tube diameter $D$ as $\beta/D^2$, with the coefficient $\beta$ depending on the chiral angle. The armchair tubes preserve conductivity, since their bands $E^A_{\mathcal{A}}(k)$ and $E^B_{\mathcal{A}}(k)$ cross in the new point $k_{\mathrm{F}} = (2/a)\arccos(V_3/2V_1) < 2\pi/3a$.

To conclude, only for the armchair tubes the bands yielding the conductivity within the simplest tight binding model have different set of the conserved quantum numbers. The difference, the opposite vertical mirror parity, can be observed only with help of the full symmetry line group. In the view of the non-crossing rule, exclusively armchair tubes conductivity is preserved, as illustrated by more exact model. Regularity in the width of the opened gap in $\mathcal{C}$ and $\mathcal{Z}$ tubes, as well as the shift of $k_{\mathrm{F}}$ in $\mathcal{A}$ tubes, can be used to resolve some ambiguities in the tubes identification. It should be emphasized that the established complete set of bands quantum numbers enables to calculate exhaustive set of selection rules for the various processes involving interband transitions. In this context it is relevant that the point $k_{\mathrm{F}}$ given in the table 1 becomes weak van Hove singularity for $\mathcal{C}$ and $\mathcal{Z}$ tubes in the presented model. Concerning $\mathcal{A}$ tubes, the new crossing point carries nontrivial helical $\tilde{k}$ and total angular momentum $n\hbar$, although the "pure" angular momentum vanishes; this property of the conducting band profoundly confirms proposed chirality of the currents [16].

## References


[1] S. Iijima, Nature, **354**, 56 (1991).

[2] M. S. Dresselhaus, Nature, **391**, 19 (1998); P. L. McEuen, Nature **393** 15 (1998).

[3] N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett. **68**, 1579 (1992).

[4] M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1998.

[5] C. T. White, D. H. Robertson and J. W. Mintmire, Phys. Rev. B **47** 5485 (1993); J. W. Mintmire and C. T. White, Phys. Rev. Lett. **81** 2506

(1998).
[6] R. A. Jishi, L. Venkataraman, M. S. Dresselhaus and G. Dresselhaus, Phys. Rev. B, **16** 11176 (1995); C. T. White, T. N. Todorov, Nature **393**, 240 (1998); H. J. Choi and J. Ihm, Solid State Com., **111**, 385-90 (1999).
[7] M. Damnjanović, I. Milošević, T. Vuković and R. Sredanović, Phys. Rev. **B 60** 2728-39 (1999); J. Phys. A **32** 4097-4104 (1999).
[8] J. W. G. Wildoer and L. C. Venema and A. G. Rinzler and R. E. Smalley and C. Dekker, Nature, **391** 59 (1998); T. W. Odom and J.-L. Huang and P. Kim and C. M. Lieber, Nature, **391** 62 (1998).
[9] C. Kane and E. J. Mele, Phys. Rev. Lett. **78** 1932-5 (1997).
[10] M. Damnjanovic, T. Vuković and I. Milošević, J. Phys. A (to appear)
[11] S. L. Altmann, *Band Theory of Solids. An introduction from the Point of View of Symmetry* (Clarendon Press, Oxford, 1991).
[12] I. Milošević and M. Damnjanović, Phys. Rev., **B 47** 7805 (1993).
[13] L. Landau and E. M. Lipshic, *Quantum Mechanics* (Pergamon, London, 1958).
[14] W. A. Harrison, *Electronic Structure and the Properties of Solids* (San Francisko, Freeman, 1980). Inverse square dependence of the interatomic element $V$ on the interatomic distance $d$ results in linear dependence of $\Delta V$ on the variation of the distance.
[15] S. Tasaki, K. Maekawa and T. Yamabe, Phys. Rev. B **57** 9301 (1998).
[16] Y. Miyamoto, S. G. Louie, M. L. Cohen, Phys. Rev. Lett. **76** 2121 (1996)